

5,6-DIMETHOXY-7,3',4'-TRIHYDROXYFLAVONE FROM *ANISOMELES OVATA*

L. JAGAN MOHAN RAO, G. N. KRISHNA KUMARI and N. S. PRAKASA RAO*

Department of Chemistry, Nagarjuna University, Nagarjunanagar, 522 510 Andhra Pradesh, India

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Key Word Index—*Anisomeles ovata*; Labiatae; flavone; 5,6-dimethoxy-7,3',4'-trihydroxyflavone.

Abstract—5,6-Dimethoxy-7,3',4'-trihydroxyflavone was isolated from the aerial parts of *Anisomeles ovata* and characterized by both physical and chemical methods.

INTRODUCTION

Continuing our investigation [1-3] of *Anisomeles ovata* we now report the isolation of 5,6-dimethoxy-7,3',4'-trihydroxyflavone (**1**) from the aerial parts. Methylation of a 5-hydroxyl leaving the 7-hydroxyl free in 5,7-dihydroxylated flavones is rare. Of the vast majority of flavones reported so far, such compounds have been found only three or four times. This is the second such report from the Labiatae [4].

RESULTS AND DISCUSSION

From the alcoholic extract of aerial parts of *Anisomeles ovata* **1** ($C_{17}H_{14}O_7$, mp 295-297°) was separated by chromatographic methods. It gave a positive Shinoda test for a flavone and a positive ferric chloride reaction. It yielded a pentamethoxyflavone on methylation with dimethyl sulphate and potassium carbonate in acetone. The reaction time (4 hr) indicates the lack of a 5-hydroxyl group. The pentamethyl ether is identical with 5,6,7,3',4'-pentamethoxyflavone by comparison with an authentic sample. The 1H NMR spectrum of **1** at 270 MHz showed the presence of two methoxyl groups at δ 3.80 (3H, s) and 3.96 (3H, s). The B-ring protons are observed at δ 6.92 (1H, d, $J = 8$ Hz), 7.42 (1H, d, $J = 3$ Hz) and 7.45 (1H, q, $J = 8, 3$ Hz). The signal at δ 6.84 (1H, s) is assigned to H-3. The only other signal at δ 6.65 (1H, s) is assigned to H-8. The placement of the two methoxyl groups is obtained from the analyses of UV and mass spectral data. The molecular ion M^+ 330 (100%) supported a dimethoxytrihydroxyflavone system. The fragment ion at m/z 315 $[M - Me]^+$ located one of the methoxyls at C-6 [5]. The ion at m/z 181 $[A - Me]^+$ allocated the other methoxyl to the A-ring. The UV spectrum of **1** showed a bathochromic shift ($\Delta\lambda$ 10 nm) of band II on addition of sodium acetate indicating a free 7-hydroxyl group [6]. The bathochromic shift of $\Delta\lambda$ 56 nm observed for band I on addition of aluminium chloride which disappeared on hydrochloric acid addition, indicated the presence of an *ortho*-dihydroxy system in the B-ring and the absence of a free 5-hydroxyl [6]. The lack of a low field signal in the 1H NMR spectrum beyond δ 10 and its easy methylation supports the lack of

a free 5-hydroxyl, allocating the other methoxyl to C-5. The *ortho*-dihydroxy system in the B-ring is also supported by UV, from the bathochromic shift ($\Delta\lambda$ 26 nm) of band I on addition of sodium acetate and boric acid when compared to the methanol spectrum. Hence, **1** is 5,6-dimethoxy-7,3',4'-trihydroxyflavone.

EXPERIMENTAL

Plant material of *Anisomeles ovata* R. Br. was collected near Mangalagiri (A.P. India) in December 1980. The powdered aerial parts (5 kg) were extracted with hexane and MeOH successively. The MeOH extract was concd and extracted into C_6H_6 , Me_2CO and MeOH fractions. The Me_2CO fraction was chromatographed on Si gel using C_6H_6 and C_6H_6 - Me_2CO mixtures. The new flavone (5 mg) was obtained from the C_6H_6 - Me_2CO (17:3) fraction and recrystallized from MeOH to give yellow powder, mp 295-297°. UV λ_{max}^{MeOH} nm: 344, 273, 254sh, 210; NaOMe: 390, 265, 225; $AlCl_3$: 400, 301sh, 275, 214; $AlCl_3 + HCl$: 362, 283, 260sh, 212; NaOAc: 400, 270, 220; NaOAc + H_3BO_3 : 370, 262, 220. 1H NMR ($DMSO-d_6 + CD_3OD$): δ 3.80 (3H, s, OMe), 3.96 (3H, s, OMe), 6.65 (1H, s), 6.84 (1H, s), 6.92 (1H, d, $J = 8$ Hz), 7.42 (1H, d, $J = 3$ Hz), 7.45 (1H, q, $J = 8, 3$ Hz). MS m/z (rel. int.): $[M]^+$ 330 (100%), 315 $[M - Me]^+$ (72), 299 $[M - OMe]^+$ (7), 287 $[M - COMe]^+$ (24), 313 $[M - OH]^+$ (12), 181 $[A - Me]^+$ (10), 153 $[A - COMe]^+$ (10), 137 $[B\text{-ring}]^+$ (4). Methylation of **1** (Me_2SO_4 , Me_2CO , K_2CO_3 , 4 hr) yielded 5,6,7,3',4'-pentamethoxyflavone, mp 178-179°.

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*Author to whom correspondence should be addressed.